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              FEB 54   J R REITZ, S R ASPINALL

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OFFICE OF NAVAL RESEARCH
London

EUROPEAN SCIENTIFIC NOTES

15 February 1954   No. 8 - 4

AMERICAN EMBASSY   LONDON, ENGLAND

PROTON RESONANCE STATES IN Si^{28}

At the University of Glasgow Drs. J. G. Rutherglen, P. J. Grant and co-workers, using the 800 kev cascade generator, have been investigating the resonances and gamma rays involved in the capture of protons by Al^{27}. A scintillation spectrometer and multiple channel kick-sorter have been used both in the investigation of the gamma ray energies and in a determination of the angular distribution of the gamma radiation with respect to the direction of the incident protons. Alpha particles from the reaction $Al^{27}(p,\alpha)Mg^{24}$ have also been measured. The target thickness is 5 - 10 kev. Preliminary results of this study have been published (Proc. Phys. Soc. 66, 800 (1953)), but more recent results are summarized in the following table, where YES or NO indicates the

Resonance kev / Radiation	404	503	630	652	677
α	NO	YES	YES	NO	NO
γ 12Mev	NO	YES Isotropic	NO	Extremely little	NO
γ 10.4Mev	Very Little	YES Isotropic	YES $1-0.11\cos^2\theta$	YES $1-0.48\cos^2\theta$	YES Isotropic
γ 7.5Mev	YES $1+0.31\cos^2\theta$	YES	YES $1+0.10\cos^2\theta$	YES $1-0.12\cos^2\theta$	YES
γ 1.8Mev	YES	YES	YES $1+0.13\cos^2\theta$	YES	YES

presence or lack of the radiation in question, and θ denotes
the angle of emission of the radiation with respect to the
direction of the incident proton. From this table, a level
diagram for the states of Si^{28} can be constructed as shown
in Figure 1.

Resonances

677 kev	12.25 Mev		J=3, +
652	12.23		2 −
630	12.21		3 −
503	12.09		2 +
404	11.99		4 −

7.1

5.2 ⎫ J = 3 and
4.6 ⎬ either 2 or 4

1.8   2 +

0   J = 0, +   Si^{28}
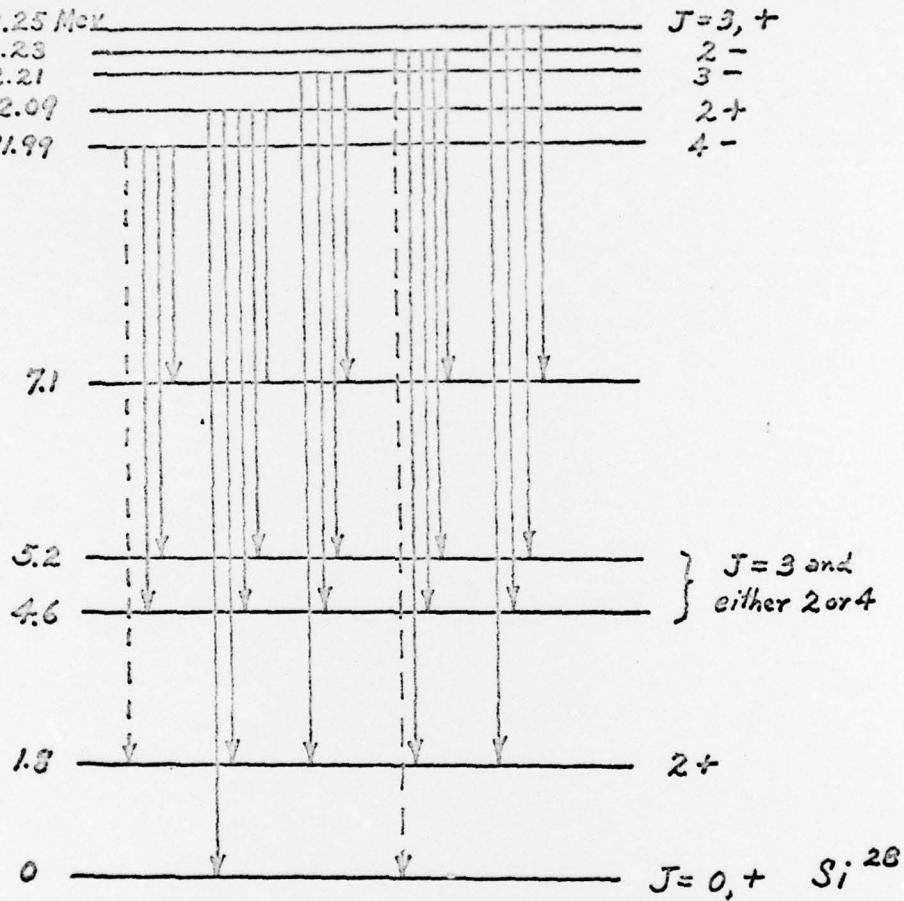
Fig. 1. Level Diagram from Al^{27}(p,γ)Si^{28} and Al^{27}(p,α)Mg^{24}.

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From the table it is seen that alpha particles are emitted in the 503 and 630 kev proton resonances but not in the others. The corresponding compound states are therefore probably either 2+ or 3-. (The ground state of Mg^{24} is J = 0, + and that of Al^{27} is $d_{5/2}$). The angular distributions of the gamma radiations suggest that the 630 kev state is odd and the 503 kev state even parity. This agrees with the relative strength of the ground state transitions. The 677 kev state which emits gamma rays isotropically is probably 3+ (Magnetic dipole radiation to the 2+ state). The angular distributions and relative intensities then give the assignment of 4- to the 404 kev level and 2- to the 652 kev level.
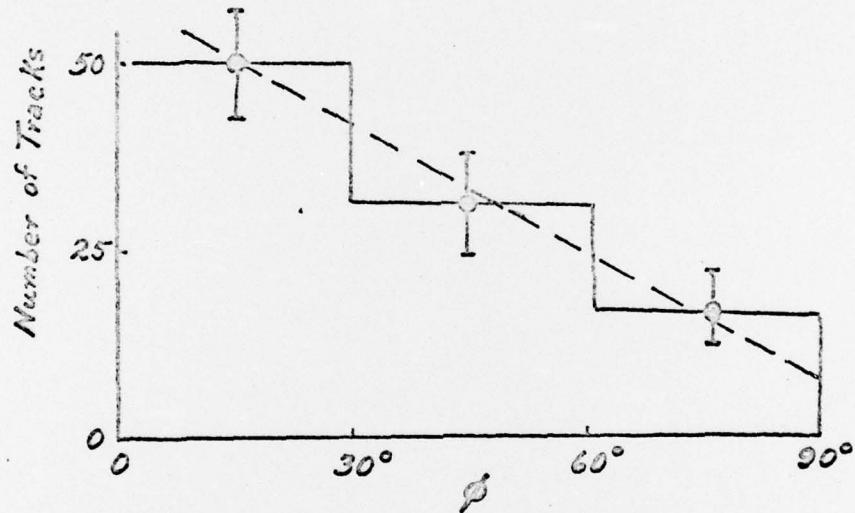
Fig. 2. Angular Distribution of Photoprotons.

An interesting technique has been used by the nuclear emulsion group at Glasgow to confirm the supposition that the 10.4 Mev radiation from the 652 kev resonance is in fact electric dipole in character. Dr. H. Muirhead and Mr. I. S. Hughes have impregnated 200μ nuclear emulsions with D_2O until a four- or five-fold increase in volume is obtained. Then these emulsions are exposed to the gamma radiation in question for about 500μa-hours of

proton bombardment of aluminum. The photoprotons having a
range appropriate to the photodisintegration of deuterium
by 10.4 Mev gamma radiation are observed, and their distri-
bution in angle $\emptyset$ is recorded. $\emptyset$ is the angle which the
track of the photoproton makes with respect to the plane
containing the paths of the original bombarding proton and
the gamma ray. Because of the poor statistics in this type
of work the tracks are lumped into regions of 0°-30°, 30°-
60°, and 60°-90°. The results are shown in Figure 2 where
the theoretical curve for electric dipole radiation is
shown as a dotted line. The effect is quite large for this
radiation because of the large asymmetry in the original
angular distribution of the gamma rays, and the result is
consistent with the assumed transition 2- to 2+.

APHID PIGMENTS

As part of a systematic chemical investigation of
insect constituents, Prof. A. R. Todd and Dr. A. W. Johnson
at the University of Cambridge are conducting an interest-
ing program on the isolation and structure determination of
the characteristic pigments found in certain species of
aphids. Two varieties of aphid pigments have been studied
in detail. One is derived from A. fabae, which is found on
bean plants, and the other from T. salignus, which infests
willow trees. The problems inherent in obtaining suf-
ficient material for study can be appreciated when it is
realized that the individual insect weighs less than 0.5 mg
and the percentage of pigment varies from 0.2 to 2.0 per
cent of the body weight. However, the collection program
is so efficient that experiments are possible on multigram
samples.

The pigment derived from the bean aphid has been
most carefully studied. As isolated, the pigment is com-
bined with glucose to form the intensely colored protoaphin-
fb glucoside; by enzymatic degradation, xanthoaphin-fb is
produced. Acidification under mild conditions leads to
chrysoaphin-fb, which on treatment with strong acid forms
erythroaphin-fb in accordance with the accompanying diagram.
The molecular formulas of the last three products have been
determined and appear to represent successive dehydrations.

Protoaphin-fb glucoside

$\downarrow$ enzymes

Xanthoaphin-fb ($C_{30}H_{28}O_{11}$)

$\downarrow$ dilute acid

Chrysoaphin-fb ($C_{30}H_{24}O_9$)

$\downarrow$ vigorous acid treatment

Erythroaphin-fb ($C_{30}H_{22}O_8$)
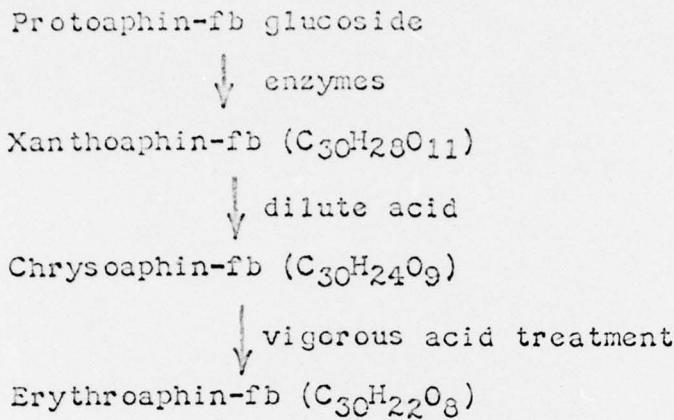
Most of the chemical work has been directed to erythroaphin-fb. Pyrolyses with zinc dust (according to the modified technique of Clar) were carried out on 300 individual batches and afforded, after extensive chromatography of the combined hydrocarbon fraction, a series of polycyclic hydrocarbons. These were identified by micromethods (principally by UV spectra) as being alkyl derivatives of perylene, benzperylene and coronene. Strong oxidation of erythroaphin-fb with nitric acid produces mellitic acid.

Of the eight oxygens in erythroaphin, two are considered to be in the form of a quinone on the basis of spectral and chemical evidence. Two other oxygens have been shown to be hydroxylic in nature, since diacyl derivatives have been prepared. A Kuhn-Roth oxidation indicated the presence of two C-methyl groups. Qualitative tests for peroxide or acetal linkages were negative and the remaining four oxygens are assumed to be present as ethers on the basis of their chemical nonreactivity. Methoxyl and ethoxyl tests are negative even to special modifications of the Zeisel method which have been developed recently.

Erythroaphin-fb reacts readily with ammonia, primary and secondary amines. The reaction products are best explained by assuming addition to the quinone system followed by auto-oxidation or disproportionation. Bromine reacts rapidly with erythroaphin-fb to yield a substitution product containing unreactive bromine.

On the basis of these data, Todd and Johnson suggest a tentative formula for erythroaphin-fb which is

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erythroaphin-fb (tentative)
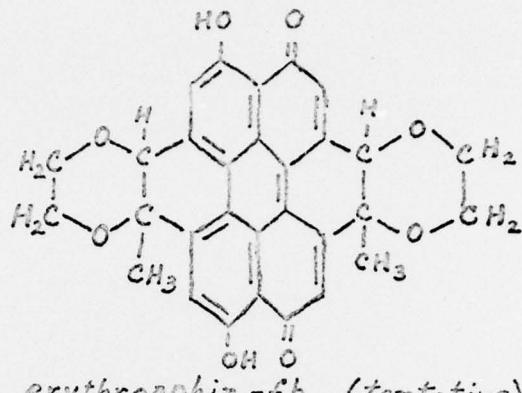
in accord with all of the known observations. It will be noted that this formula is remarkable in a number of ways. No other known natural product is a derivative of perylene quinone, and the partially hydrogenated coronene nucleus is also novel. It is apparent that a rather complicated oxidation-reduction system could be based on this formula and it is possible that such processes could play an important role in the insect's metabolism. The presence of the pigment to the extent of as much as 2 per cent of body weight makes this suggestion more attractive.

The closely related pigment series derived from the willow aphid, T. salignus, appears to differ mainly in the stereoisomerism. The amino derivatives of erythroaphin from both series can be converted by zinc and acid treatment to the identical substance, which is erythroaphin-fb. It appears that the change undergone by the willow aphid erythroaphin as a result of these reactions is an epimerization at the carbon in the dioxane ring which is attached to the quinone and which carries a single hydrogen. This structure for erythroaphin permits the construction of formulas for chrysoaphin-fb and xanthoaphin-fb by successive hydrations of the double bonds in the perylene quinone system. The syntheses of various degradation products, including the alkylated hydrocarbons derived from the zinc dust distillation, are in progress.


NATURAL POLYACETYLENES

The polyacetylene structure has been found in natural products of a surprisingly wide variety and distribution. Polyacetylenes have been isolated from plants of the Compositae family (Sörensen, Chem. and Ind. 240 (1953)),

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and have also been found in plant poisons and in seed oils. The antibiotic, mycomycin, is elaborated by a soil actinomycete, and certain fungi (Basidiomycetes) also furnish compounds with a conjugated triple bond system.

The isolation from microbiological sources of the highly unsaturated antibiotic, agrocybin, has been reported recently (Kavanaugh, Hervey, and Robbins, Proc. Nat. Acad. Sci., 36 102 (1950)). A group under the direction of Prof. E.R.H. Jones (Manchester University) was able to assign to it the structure octa-2,4,6-triynamide (Jones and Bu'Lock, J. Chem. Soc. 3719 (1953)). The ultraviolet absorption spectrum was characteristic of a conjugated triacetylene, and the infrared spectra revealed the presence of an unsubstituted amide. Quantitative microhydrogenation required six moles of hydrogen and yielded a product shown to be n-octanamide by comparison with an authentic sample.

The synthesis of agrocybin has more recently been accomplished by the following sequence of reactions:

$$CHO + HC \equiv C-C \equiv C-CH_2OH \xrightarrow{\text{via}} CH_3CHC \equiv C-C \equiv C-CH_2OH \longrightarrow$$

$$\overset{|}{OH}$$

Grignard
Synthesis

$$CH_3CHC \equiv C-C \equiv C-CH_2Cl \longrightarrow CH_3C \equiv C-C \equiv C-C \equiv CH \xrightarrow[\text{(2) } CO_2]{\text{(1) Grignard}}$$

$$\overset{|}{Cl}$$

$$CH_3C \equiv C-C \equiv C-C \equiv CCO_2H \xrightarrow[\text{(2) } NH_3]{\substack{\text{(1) Methyl-} \\ \text{esterification}}} CH_3C \equiv C-C \equiv C-C \equiv CCONH_2$$

agrocybin
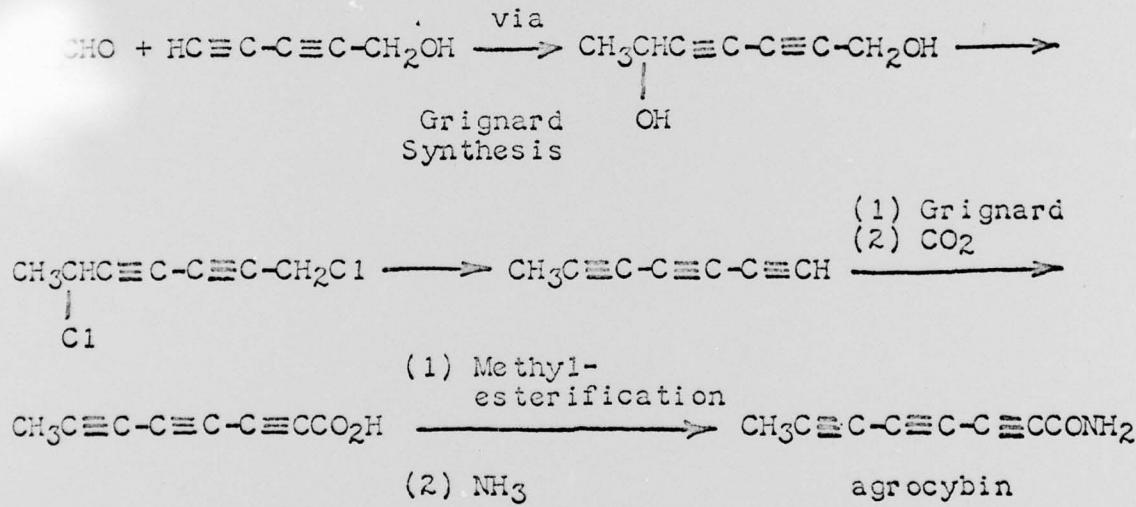
Penta-2,4-diyn-1-ol was converted to the Grignard derivative and condensed with acetaldehyde. The resulting diacetylenic glycol was transformed to the dichloro derivative, which was dehydrohalogenated to yield hepta-1,3,5-triyne. Conversion to the Grignard derivative followed by carbonation gave the acid. The corresponding amide, prepared via the methyl ester proved to be identical to natural agrocybin.

This determination of structure and synthesis is a good example of how Prof. Jones' experience in the synthesis of polyacetylenic compounds reinforces the study of similar natural products.

PHYSICAL CHEMISTRY RESEARCH AT NEWCASTLE

The wide variety of problems which are being investigated in the Physical Chemistry Department at King's College, Newcastle upon Tyne, include a study of electrode processes, the properties of solutions (particularly those of hydrogen peroxide), and various problems on the nature of carbon and coal. This research is directed by Prof. W.F.K. Wynne-Jones, although the last-mentioned work on carbon is more directly under the supervision of Dr. H. A. Blayden in the Northern Coke Research Laboratories of the British Coke Research Association located in the Department. The work of this Department is discussed in some detail in Technical Report ONRL-3-54; some of the research on electrode processes and the determination of paramagnetic resonance in zethrene are discussed below.

Electrode Processes

The main feature of the Newcastle approach to the study of electrode reactions is that electrochemical and structural methods are combined to yield maximum information. Metals under study are lead (see below), nickel, manganese, mercury, and silver. The recent observation by Dr. H. R. Thirsk on the reactions of a liquid mercury surface with HCl and with H_2SO_4, while exposed to a potential difference, are noteworthy. With hydrogen chloride, a coherent calomel film of about $80 - 100A^o$ thickness is formed which gives a beautiful single crystal pattern in electron diffraction. Apparently nucleation occurs on small hexagonal regions followed by oriented growth. In the case of sulfuric acid, nucleation is apparently much faster than the subsequent growth process, mercurous sulfate powder being formed on the surface (cf. Proc. Phys. Soc. 366, 129 (1953)).

The Behavior of the Lead Dioxide Electrode

The behavior of the lead dioxide electrode has been elucidated by the researches of W. H. Beck, R. Ling, and W.F.K. Wynne-Jones. A thermodynamic analysis of the effects

of variations of temperature, pressure, and concentration of electrolytes upon the electromotive force of the lead storage cell definitely shows that in the cell one mole of sulfuric acid is consumed and one mole of water is produced per Faraday. Thus the double sulfation theory first proposed in 1882 is the correct one for this system. As will be recalled, according to this theory the cell reaction is

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O$$
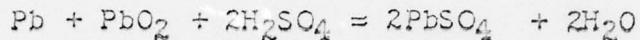
The most conclusive evidence in favor of this theory, according to the Newcastle workers, is that it correctly predicts the observed linear dependence of the electromotive force on acid concentration.

The irreversible discharge of the lead storage cell was studied under various conditions, and it was concluded that the reaction mechanism remains the same as for the reversible electrode. In these investigations freshly plated lead surfaces of accurately known apparent area were anodically polarized under conditions of constant current density. The fact that the potential-time and potential-log current density curves for the lead electrode have forms which are very similar to those for the lead dioxide electrode is an additional interesting observation which strongly suggests that the same factors determine the dependence of potential on time and on current density for both electrodes.

An important conclusion reached by Wynne-Jones and collaborators is that the detailed mechanism, by which the charging and discharging of a lead dioxide electrode occurs, can contain no non-electrochemical stage in which equilibrium is impossible. This is rigorously true under reversible conditions, and the observed overpotential characteristics indicate that it also applies to the lead storage cell under normal discharge conditions.

Paramagnetic Resonance in Zethrene

A recent determination of the paramagnetic resonance of zethrene supports a free radical formulation for this polycyclic hydrocarbon. Dr. E. Clar (Glasgow) proposed such a structure for this compound at Stockholm last August (cf. ESN 7, 233 (1953)) and through the cooperation

of Dr. J. Weiss (Newcastle) the paramagnetic resonance absorption of one of his samples was recently determined in the laboratory of Dr. E. E. Schneider (Physics Department, Newcastle). At a resonance frequency of 9405 Mc/sec the width of the absorption band is 13.0 ± 0.5 gauss at the half-height. The Landé splitting factor, g = 2.004 ± 0.001. Within experimental error the material behaves precisely as diphenylpicrylhydrazyl, and represents most probably another case of spin paramagnetism.

PRESTON'S METHOD OF MEASURING TURBULENT SHEAR

Dr. J. H. Preston of the Cambridge University Aeronautics Laboratory has developed a very simple method for measuring turbulent shear. This method is based on the similarity law for the average-velocity profile in a turbulent boundary layer,

$$u/U_\tau = f(U_\tau y/\nu),$$

and amounts simply to the measurement of the pressure difference with a pitot which rests flush on the surface in question. Here

$$U_\tau = \sqrt{\tau_0/\rho}$$

is the friction velocity, ν is the kinematic viscosity of the fluid (assumed constant), y is the vertical distance from the surface, τ_0 is the turbulent shear stress at the surface, and ρ is the density of the fluid.

On the basis of the law for the velocity profile, a relation of the form

$$\Delta p \cdot d^2/\rho \nu^2 = F(\tau_0 d^2/\rho \nu^2)$$

may be expected to be valid, where Δp is the pressure difference as measured by the pitot, and d is the diameter of the pitot tube. Calibration of the pitot tube or of a series of geometrically similar pitot tubes yields the function desired which may then be used to derive shear stresses at the surface from measurement of the pitot pressure difference.

This method is described in a British Aeronautical Research Council memorandum 15,758 F.M.1883 and is to appear in the Journal of the Royal Aeronautical Society. Additional details and comments are given in Technical Report ONRL-10-54.

TECHNIQUE EMPLOYED ON MOUNT EVEREST FOR MEASURING RESPIRATORY EXCHANGES

At the December meeting of the Physiological Society in London, Dr. L.G.C.E. Pugh, physiologist on the British Everest Expedition of 1953, demonstrated the technique used on Everest to determine respiratory exchanges.

The method of collecting expired air during work requires the subject to start the test carrying on his back an empty Douglas bag of 100, 200, or 300 l. capacity made of light weight, rubber-coated linen fabric (Dunlop) and weighing one to two pounds. The empty bag which is closed with a clamp is connected with a low-resistance valve box via a two-foot length of one inch internal diameter alkathene tube bent in a curve to pass over the subject's head from the valve unit to the bag carried on his back. The subject, wearing a nose clip, holds the valve box in front of his face ready to place the mouthpiece in his mouth at a signal. After five minutes work, the signal is given to start collecting. This is done at the end of an expiration so that the subject has the next inspiration in which to place the mouthpiece in his mouth and the assistant has this amount of time to remove the clamp from the neck of the bag. Expired air is collected until the bag is full, pressure building up rapidly until further expiration becomes difficult. At a second signal at the end of an expiration, the assistant clamps the neck of the bag and the subject removes his mouthpiece. Time elapsing between the two signals is recorded by stopwatch.

After the bag has stood for some minutes to allow its contents to cool to near ambient temperature, the pressure of the expired air in the bag is measured with an aneroid manometer. After taking a sample for analysis the clamp is then released and a Casella thermometer is thrust as far as possible up the neck of the bag. The air is allowed to escape slowly and its temperature is measured over 1 min as it flows along the neck of the bag. Using

these data, the volume of the expired air is read directly from appropriate tables.

The chief source of error lies in the measurement of temperature, although this error is not likely to exceed 2 - 3°C which will only affect the volume measurement by 1 per cent. The fact that the last two or three respirations are made against increasing resistance may introduce a slight error in the measurement of small volumes, but this effect is negligible when such large bags are used. It is not always feasible to allow the expired air to cool to ambient temperature, particularly if the bag has not been inflated tightly enough and becomes flaccid as it cools.

OPEN-CIRCUIT OXYGEN EQUIPMENT USED BY THE BRITISH MOUNT EVEREST EXPEDITION

At the same meeting of the Physiological Society, Dr. J. E. Cotes described the Everest oxygen equipment, which was of a type similar to that introduced in the Royal Air Force in 1940 and used by them throughout the greater part of the war.

Oxygen from a high-pressure cylinder is fed at a constant rate through a reducing valve and flow regulator into an 'economizer', whence it is ejected into the oxygen mask during inspiration to enrich the air which the subject breathes. During expiration the oxygen fills up the economizer bag. The opening pressure differential of the air-mix inspiratory valves on the mask is adjusted to exceed the pressure differential needed to start the discharge of oxygen from the economizer. The subject initially breathes pure oxygen until the 'economizer' is exhausted, and then inspires atmospheric air. Thus no oxygen is expended in enriching the dead space air. The oxygen contained in the expired air is wasted to the atmosphere.

Of the component items of equipment some were made specially, others were modified from standard items. They are assembled to form disposable cylinder units each containing 660 1. of oxygen. Up to three units mounted on a light-weight carrying frame supplied low-pressure oxygen to the economizer. The oxygen mask was modified from a standard R. A. F. item by fitting different valves and a protective rubber cowl. It had an acceptable flow resistance for maximal effort as defined by C. B. McKerrow

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(1953, Proc. XIXth Int. Physiol. Congr., p. 605), and did
not freeze up when worn at -25°C in a 25 m.p.h. wind at
ground-level for 1½ hr. There were also soft rubber masks
for night use. Oxygen delivery rates of 1-5 S.T.P. l./min
were provided. The intention was to raise the oxygen
tension of the air breathed from that obtaining at 28,000
ft. to that at 21,000 ft., the altitude to which the sub-
ject was acclimatized (H. L. Roxburgh, 1947, Geogr. J. 109,
207). Greater flows, while increasing climbing ability,
would have exposed the subject to the danger of losing the
benefits of acclimatization.

INTERNATIONAL CONFERENCE ON SEMICONDUCTORS

An International Conference on Semiconductors will
be held in Amsterdam on 29 June - 3 July 1954 under the
auspices of the Netherlands Physical Society with the
support of the IUPAP and UNESCO. This conference will
immediately precede the IUPAP meeting in London, and will
precede by two weeks the conference on Defects in Crystal-
line Solids at Bristol. Topics of the Conference will
include: recombination in semiconductors, an analysis of
the band approximation in solids; impurity centers, photo-
conductivity and luminescence, and the preparation of semi-
conductors in a reproducible manner.

Those wishing to attend the conference should
apply to the Secretary, Dr. H. J. Vink, Floralaan 142,
Eindhoven, Holland, for further information. Early appli-
cation is encouraged, the closing date being 1 June 1954.

SIXTH INTERNATIONAL ASTROPHYSICAL SYMPOSIUM

The Sixth International Astrophysical Symposium
will be held in Liège, Belgium, on 15 - 17 July 1954 on the
subject "Solid Particles in Astronomical Objects". The
Symposium has been organized by the Institut d'Astrophysique,
Liège; Prof. O. Struve, President of the International
Astronomical Union has agreed to act as chairman. Subjects
to be discussed at the conference are: (1) dust in the solar
system, (2) dust phenomena and related spectra in stars,
(3) laboratory investigations on graphitic particles and
related spectra, (4) smoke in interstellar space and in
nebulae, and (5) dust and the origin and evolution of stars.

DISCUSSION ON COAGULATION AND FLOCCULATION

A General Discussion of the Faraday Society will be held from 15 - 17 September 1954 at Sheffield University on Coagulation and Flocculation. The Discussion is being arranged by the Colloid and Biophysics Committee of the Faraday Society and will deal with three main topics: (1) Kinetics and Energetics of Collision and Adhesion in True Colloids, (2) Processes in More Coarsely Dispersed Systems, and (3) Coagulation and Specific Interaction in Soaps and Biological Systems.

DISCUSSION ON NUCLEAR CHEMISTRY

The Annual Discussion of the Bunsen Society will be devoted to nuclear chemistry this year. It is scheduled for 27 - 30 May in Bayreuth and is being organized by Professors W. Groth (Bonn) and J. Mattauch (Mainz).

PROCEEDINGS OF THE KJELLER CONFERENCE ON HEAVY WATER REACTORS

The Proceedings of the Kjeller Conference on Heavy Water Reactors, held on 11 - 13 August 1953 under the auspices of JENER, are now available at 35 Norwegian kroner per copy. The Proceedings have been edited by J. A. Goedkoop and G. Jenssen, are paper-bound with 238 pages, and are identified as JENER Publication No. 7. Copies may be ordered from: The Librarian, JENER, Kjeller per Lilleström, Norway; checks are to be made payable to: The Joint Establishment for Nuclear Energy Research, Kjeller per Lilleström, Norway.

PERSONAL NEWS ITEMS

C. H. Longuet-Higgins, Professor of Theoretical Physics at King's College, London, has been appointed Professor of Theoretical Chemistry at Cambridge University in succession to Sir John Lennard-Jones.

G. Temple, formerly Professor of Mathematics at King's College, London, has recently assumed duties as Sedleian Professor of Natural Philosophy, Oxford University. His mail address is the Mathematical Institute, Oxford University, Oxford.

<u>TECHNICAL REPORTS OF ONRL</u>

The following reports have been forwarded to ONR, Washington. Copies may be obtained by addressing requests to the Commanding Officer, Office of Naval Research Branch Office, Navy No. 100, c/o Fleet Post Office, New York, N. Y.

ONRL-142-53   "Discussion on Unimolecular Reactions" by G. J. Szasz

ONRL-1-54   "Physics and Chemistry of Surfaces" by G. J. Szasz

ONRL-2-54   "Experimental Nuclear Physics at Amsterdam and Utrecht" by J. R. Richardson

ONRL-3-54   "Physical Chemistry Research at King's College, Newcastle upon Tyne" by G. J. Szasz

ONRL-6-54   "Protective Measures in Total Body Irradiation" by J. L. Tullis

ONRL-8-54   "Transistor Research at Reading" by John R. Reitz

Prepared by the Scientific Staff
Edited by J. R. Reitz
Submitted by Dr. S. R. Aspinall
            Scientific Director

P. S. CREASOR
Captain, U.S.N.
Assistant Naval Attache for Research

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